

DEPARTMENT OF MECHANICAL ENGINEERING AND MECHANICS
COLLEGE OF ENGINEERING TECHNOLOGY
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P-37

DEVELOPMENT OF POLYSILSESQUIOXANE COMPOSITES

By

K. Srinivasan, Research Associate

and

S. N. Tiwari, Principal Investigator

Progress Report
For the period ended June 30, 1990

Prepared for
National Aeronautics and Space Administration
Langley Research Center
Hampton, Virginia 23665

Under
Research Grant NAG-1-569
Robert M. Baucom, Technical Monitor
MD-Polymeric Materials Branch

(NASA-CR-180265) DEVELOPMENT OF
POLYSILSESQUIOXANE COMPOSITES Progress
Report, period ended 30 Jun. 1990 (Old
Dominion Univ.) 37 p

CSCL 110

N90-27872

63/24 0302462
Unclas

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FOREWORD

This is a progress report on the research project, "Chemoviscosity Modeling for Thermosetting Resins," for the period ended June 30, 1990. Special attention during this period was directed to the study of "Development of Polysilsesquioxane Composites." The work was supported by the NASA Langley Research Center (Polymeric Materials Branch of the Materials Division) under the grant NAG-1-569. The grant was monitored by Mr. Robert M. Baucom.

DEVELOPMENT OF POLYSILSESQUOXANE COMPOSITES

K. Srinivasan* and S. N. Tiwari#

ABSTRACT

Polymer composites are increasingly being required to operate for prolonged durations at higher temperatures than in the past. Hence there have been increased efforts devoted to synthesizing and characterizing polymers capable of withstanding temperatures greater than 300 °C for long periods. Several such organic polymers have been investigated in recent times. This research effort seeks to enquire if inorganic polymers can be utilized to provide the same result.

Ceramics have long been recognized as providing superior thermal properties for demanding applications. However, the extremely high softening temperatures precludes their being shaped into complex shapes through melt processing techniques common to organic polymers. One approach towards solving this problem has been through the development of preceramic polymers. These are capable of being processed in the polymeric state with ease, and subsequently being pyrolyzed to ceramic structures. This experimental study is aimed at studying the feasibility of using preceramic polymers (that have not been subject to the pyrolysis step) as high performance composite matrices for high temperature applications. A preliminary study of this nature is not geared towards optimising mechanical properties suitable for such composites. Rather this study attempts to process such resins in composite form and suitably characterize their properties.

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1. MOTIVATION

Polysilsesquioxanes ($-\text{[RSi(O)}_{1.5}\text{]}_x-$) exhibit many properties that are potentially useful for composite applications, notably high temperature stability in oxygen atmospheres, good adhesion and liquid crystal type behavior for some derivatives [1, 2]. The abundant and cheap nature of the raw materials also leads to a low cost polymer. However polysilsesquioxanes frequently form intractable gels that are not amenable to prepregging and processing operations necessary for composites. Recent breakthroughs in synthetic aspects have now permitted a renewed interest in this class of polymers for advanced high temperature applications.

The synthetic chemistry aspects [3], have been handled exclusively by Dr. Richard M. Laine of the University of Washington and the description that follows here is merely intended for completeness. Catalytic redistribution of commercially available polysiloxane oligomers of the type, $-\text{[MeHSiO]}_x-$, using dimethyltitanocene, (Cp_2TiMe_2), yields a copolymer of polymethylsilsesquioxane. Gelation of the copolymer, $-\text{[MeHSiO]}_{0.3}\text{[MeSiO}_{1.5}]_{0.7}-$, is avoided by conducting the reaction in a 5:1 excess of toluene: $-\text{[MeHSiO]}_x-$ oligomer. In order to avoid the gel formation on solvent removal, the reactive Si-H bonds are converted to Si-OR bonds by alcoholysis. The resultant copolymer, $-\text{[MeORSiO]}_{0.3}\text{[MeSiO}_{1.5}]_{0.7}-$, serves as a masked form of polymethylsilsesquioxane, that provides a tractable, soluble route to the formation of silsesquioxane polymer composites. A schematic of the chemistry is provided in Appendix 1.

For the purpose of this study, a solution of the propoxy copolymer, $-\text{[MeOPrSiO]}_{0.3}\text{[MeSiO}_{1.5}]_{0.7}-$, in 1-Propanol (hereinafter PMHS) provided by Dr. Richard Laine and his associates was utilized as the starting material. This study consisted of physical characterization of the polymer, development of prepregging and subsequent processing routes and attempts at physical modifications to achieve good quality prepreg and reproducible, void free composites.

2. EXPERIMENTAL

As mentioned previously, the starting material was an oligomeric copolymer supplied in a solution of 1-Propanol. The material was received in several batches, with varying concentrations of polymer. As prepregging conditions required a 35 % solution of polymer by weight (approximately), a common first step was to concentrate the polymer solution by distilling off calculated amounts of solvent. Brookfield viscosities and densities were routinely measured as a function of solution concentration (Figs. 1 and 2).

A preliminary thermogravimetric analysis of the PMHS copolymer was undertaken, using a Perkin Elmer TGS-2, to establish the thermal stability limit of the material. The test was conducted in air at a heating rate of 10 °C/minute, and the result appears in Fig. 3. The solvent is seen to be extremely volatile, as evidenced by the weight loss that occurs in the time interval between the weighing of the specimen and the commencement of the test (approximately five minutes). Upto 100 °C, a weight loss of 59 % is seen, mostly due to solvent loss. Between 100 °C and 375 °C, the rate of weight loss shows a two stage drop, with an inflection at 275 °C. This is presumed to be due to both continued solvent loss and evolution of reaction products. Beyond 375 °C, and at a weight loss of 74 %, the curve is seen to level off. An isothermal TGA run on a dried polymer sample in air at 350 °C also showed a very stable profile upto 200 hours (Fig. 4). This was further confirmed by mass spectrometer results.

Since it is desirable to achieve prepregging at ambient conditions, the next step undertaken was to study the drying characteristics of the PMHS solution in air at room temperature. Several samples of the solution were weighed out and air dried for periods greater than 24 hours. The samples were periodically weighed till a constant weight was observed (Fig. 5). In each case a transparent film was obtained, however these films had a tendency to crack and crumble with passage of time.

These samples were then heated in air ovens at different temperatures (250 °, 285 °, 325 °, 375 ° and 400 °C) for one hour to observe film forming capabilities. However, none of the heat treated samples was

seen to maintain film forming ability, in each case a white powder was obtained.

DSC runs were carried out on each of these samples at the rate of 10 °C/minute in a DuPont 910 DSC. An air dried film, as well as samples heated upto 150 ° and 200 °C were examined. In each case barring for a high temperature exotherm, no transitions characteristic of polymers (such as T_g) were observed. Representative results are shown in Figs. 6 and 7. This implied that though some reaction and crosslinking was probably occurring (also confirmed by FTIR results), the material did not soften (or flow) in the temperature regime studied. This has unfortunate consequences regarding processing and consolidation operations.

These results notwithstanding, the PMHS copolymer was solution prepregged via the drum winding technique. Though this apparatus has been described previously [4], a brief description of the process is outlined. An AS-4 (12K, unsized) fiber tow from a free spinning unwinding creel, passes between two tension bars and onto guide spools (that align the fiber) before it enters a sealed resin reservoir. Within the reservoir the fiber tow passes through the impregnating PMHS/1-Propanol solution over an assembly of rollers. These serve to spread the fibers as it is being impregnated and ensure complete wetout. The tow exits the reservoir through a stainless steel die that squeezes the resin solution through the fiber tow, meters the amount of resin on the fiber and shapes the thickness and width of the impregnated tow. This tow is wound on a 2.5 feet diameter drum wound with a trifluoroethylene polymer release film. The entire creel - guide roll - reservoir assembly is maintained on a moving track whose translational speed is adjusted such that the impregnated tow winds on the drum to provide a continuous gap-free prepreg. The process conditions are given in Appendix 2.

In order to determine proper B-staging conditions, several pieces of the prepreg were B-staged in air ovens for one hour at the following temperatures: 150 °, 200 °, 250 °, 300 °, 350 ° and 400 °C. These samples were subject to parallel plate plastometer experiments as well as consolidation cycles of temperature and pressure in closed molds.

In a parallel plate plastometer [5], several unidirectional pieces of prepreg are tacked together and heated between the plattens of a press under pressure to determine regimes of flow in the material and hence suitable consolidation conditions. Consolidation was monitored as the thickness change during the heat - pressure cycle. Seven unidirectional pieces sized 5/8 in. by 5/8 in. were used, and the pressure employed was 300 psi. In addition to the B-staged prepreg samples mentioned above, a prepreg sample subject to no heat treatment was also examined in the plastometer. As seen in Figs. 8 and 9, virtually no flow is seen between room temperature and 400 °C.

The B-staged samples and samples subject to no heat treatment were next subject to lamination in a Pasadena hydraulic compression press. Four 3 in. X 3 in. unidirectional prepreps were tacked together and heated upto various temperatures between 250 °C and 400 °C. A pressure of 300 psi was used during the lamination cycle. Typical hold times ranged from 15 to 30 minutes. None of the samples were seen to be effectively consolidated in the different time - temperature - pressure cycles employed.

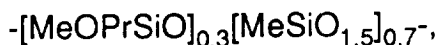
To simultaneously ameliorate the twin problems of the lack of film forming ability and potential brittleness, attempts were made to blend the PMHS copolymer with a thermoplastic polyimide. The resin selected was 5218 from Ciba - Geigy. Prominent among its properties are good toughness and high temperature resistance. Solubility tests of the PMHS copolymer were undertaken in the following solvents (to find a suitable co-solvent) : N, N-dimethyl acetamide (DMAC), N, N-dimethyl formamide (DMF), Methylene chloride, Chloroform, 1, 4-dioxane (Dioxane) and Bis (2-methoxy-ethyl) ether (Diglyme). However, the PMHS copolymer was seen to be insoluble in all these solvents. Attempts were also made to find miscibility of 1-Propanol with these solvents. Solutions of PMHS in 1-Propanol were mixed with those of 5218 in DMAC, DMF, Diglyme etc. In order to preserve the dominant properties of the polysisquioxane polymer in the mixture, the maximum blend ratios attempted were 80% polysisquioxane - 20% 5218. 90 - 10 blends were also attempted. However, in each of the above cases, the two components did not form a homogeneous mixed solution.

3. CONCLUSIONS AND RECOMMENDATIONS

Despite the attractive high temperature property profile of the Polysilsesquioxane polymer noted in this study, in its present form, several key barriers are seen as preventing its use in composite matrix applications. While the base material (70/30 masked copolymer soluble in propanol) appears to have been rendered suitable for prepregging, the conversion to the insoluble polysilsesquioxane polymer proceeds with no appreciable flow or tack. This fact is perhaps the single greatest detriment, for a failure to soften and / or flow in a low temperature regime (in this case room temperature to 400 °C) provides no avenues for effective consolidation into quality, void free laminates. Further, the tendency of the film to fall apart into a powder must also be viewed with alarm, for to fulfill its role in the composite, the resin must maintain structural and mechanical integrity, throughout the useful temperature range.

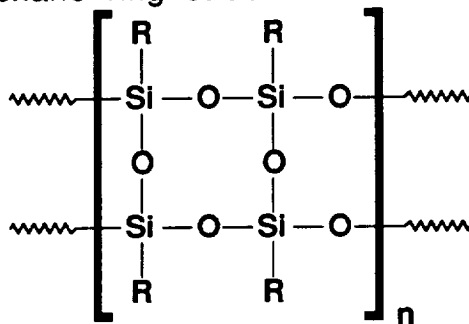
These factors notwithstanding, cost and thermal stability considerations still warrant a continued interest in this system. Several points requiring clarification, modifications and recommendations are now discussed:

1. When the general structure of the PMHS copolymer (starting material) is written as:



it is impossible to determine what a single molecule looks like. By observing a single molecule, one can readily identify potential sites for crosslinking, potential for flow *etc.* Hence it is necessary to determine the hypothesized structure of the starting copolymer, *i.e.* \bar{M}_n or \bar{M}_w of the starting copolymer.

2. The fused tetrasiloxane ring structure of the silsesquioxane:



produces a highly crosslinked structure that may be responsible for the intractable nature of the polymer generated in this study. Several modifications can be suggested to alleviate the problem. Since the above structure is generated from the unit $[\text{MeSiO}_{1.5}]$, and since that unit accounts for 70 % of the starting oligomer, a possible first step may be the reduction of the $[\text{MeSiO}_{1.5}]$ unit, *i.e.* effectively increase the extent of $-\text{[MeOPrSiO]}-$ unit in the starting oligomer. Alternatively, a fraction of the $[\text{MeSiO}_{1.5}]$ unit could be chemically modified to reduce its functionality, *i.e.* effectively reducing the cross link density in the final polymer. In both cases, not only must the chemistry be altered, but the penalty (in terms of mechanical / thermal properties of the final polymer) must also be assessed.

3. Another potential approach can be to blend / graft small quantities of film formers that can induce the polysilsesquioxane to maintain a continuous resinous network. Depending on the chemistry, these can be in resin or oligomeric / monomeric form. These can be of two basic types:

A. Silicone - Organic Polymers: Silicone - organic copolymers have been made with a variety of organic constituents [6]. Both copolymerization, as well as grafts of prepolymerized segments have been employed. Several such compositions have been used as processing aids and retain many of the excellent properties of silicone polymers. While the list of formulations is extensive and includes polyester, epoxy, phenol-formaldehyde, acrylic and ether based compositions, of importance to us, (in view of thermal and strength / stiffness properties desired), are silicone - polyimide and silicone - polycarbonate formulations. Attempts at copolymerizing or blending small quantities of these may also be attempted.

B. Silsesquioxane - Silicone Polymers: More appealing than silicone - organic copolymeric compositions, are silicone polymer modifications of the PMHS copolymer. Dimethyl, Diphenyl and Phenyl-Methyl siloxane polymers are known to possess outstanding thermal stability and good film forming properties. These resins can also be tailored to a desired property profile through control of cure catalysts and chemistry. These can not only behave as processing aids, but also provide toughness to the brittle polysilsesquioxane systems. Further, blending of the silsesquioxane polymer with silicone systems is likely to prove easier. Consideration of several factors favours the biphenyl polymer for the blending experiments. These resins possess the most

miscibility, are least brittle, have the best tack and are most thermally resistant. Further, cure chemistry can also be better controlled.

4. Finally, no discussion will be complete without a consideration of other preceramic systems. These can be broadly classified as [7]: Silicon - Carbon systems, Silicon - Nitrogen systems, Silicon - Carbon - Nitrogen systems, Silicon - Carbon - Oxygen systems and other precursor systems. Most promising among the Silicon based systems are the Polycarbosilanes. These include polymers containing both the Si - C- Si and Si - (C)_x - Si backbone. PCS-I and PCS-II are commercially available materials with an average \bar{M}_n of 1000 - 2000 and are soluble in several common organic solvents. They possess attractive thermal and mechanical properties. In the US these are available from Dow Corning, (for development purposes only), at \$ 400/kg. The search for suitable low temperature polymer fabrication routes to the ceramics of boron, aluminum and some transition metals also reveals some promising preceramic polymers such as borosiloxane polymers, carborane - siloxane polymers, boron -nitrogen polymers and organometallic aluminum and transition metal systems. Recently [8], semi-amorphous networks of sodium, potassium, lithium and magnesium silico-aluminates, (termed geopolymers), have been suggested as low temperature processible matrices for composite materials.

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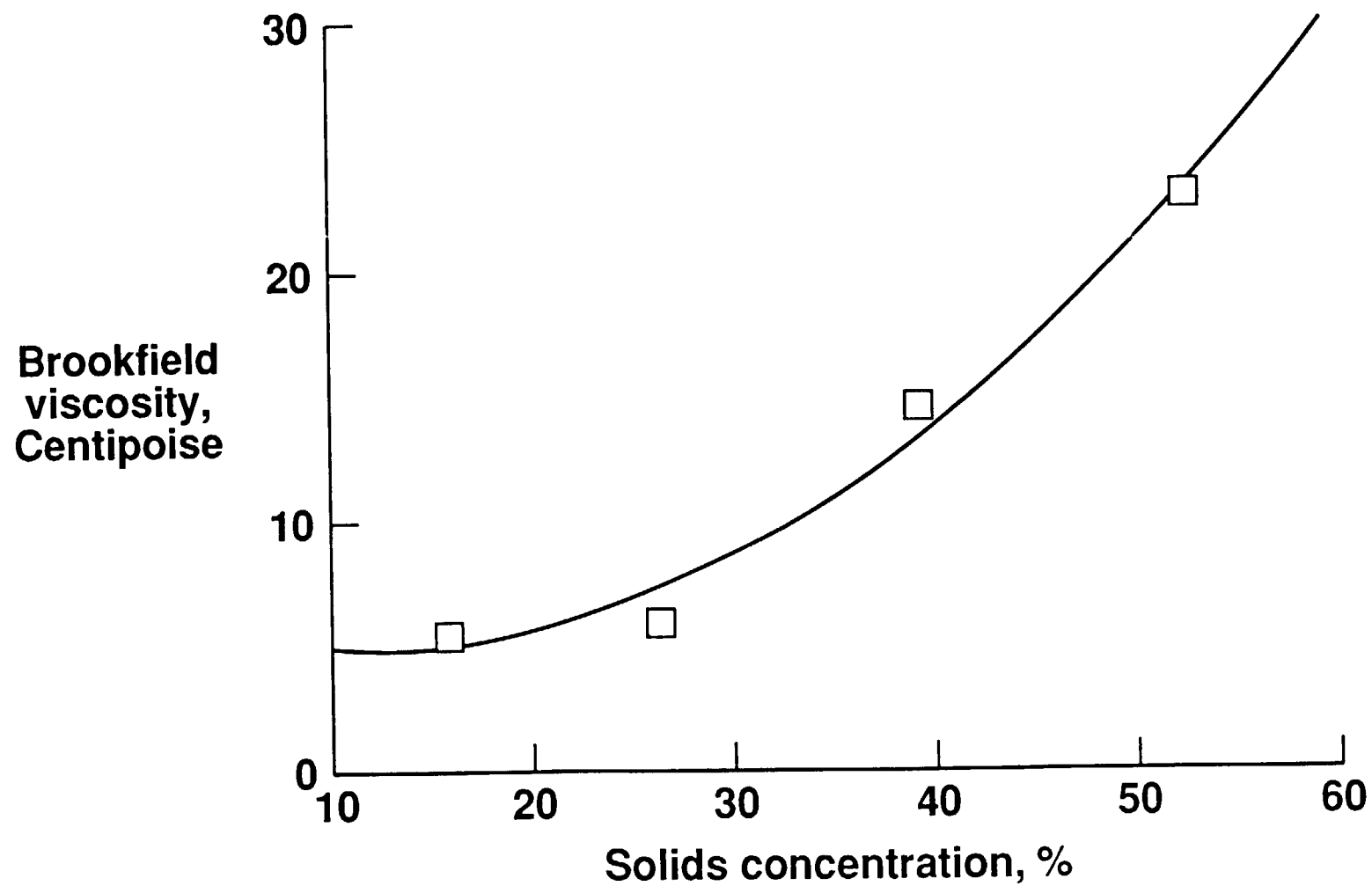


Figure 1. PMHS solution viscosity profile

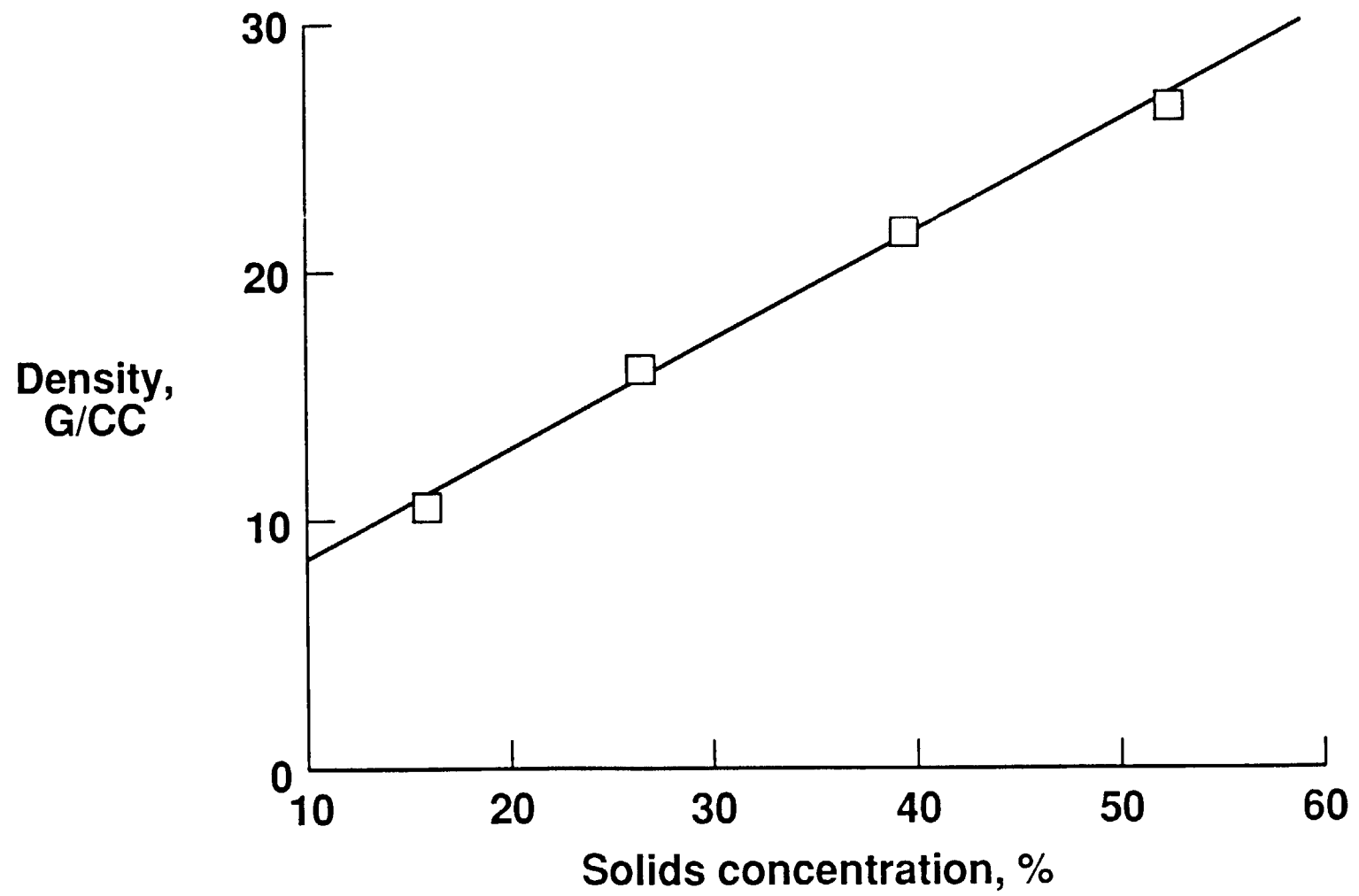


Figure 2. PMHS solution density profile

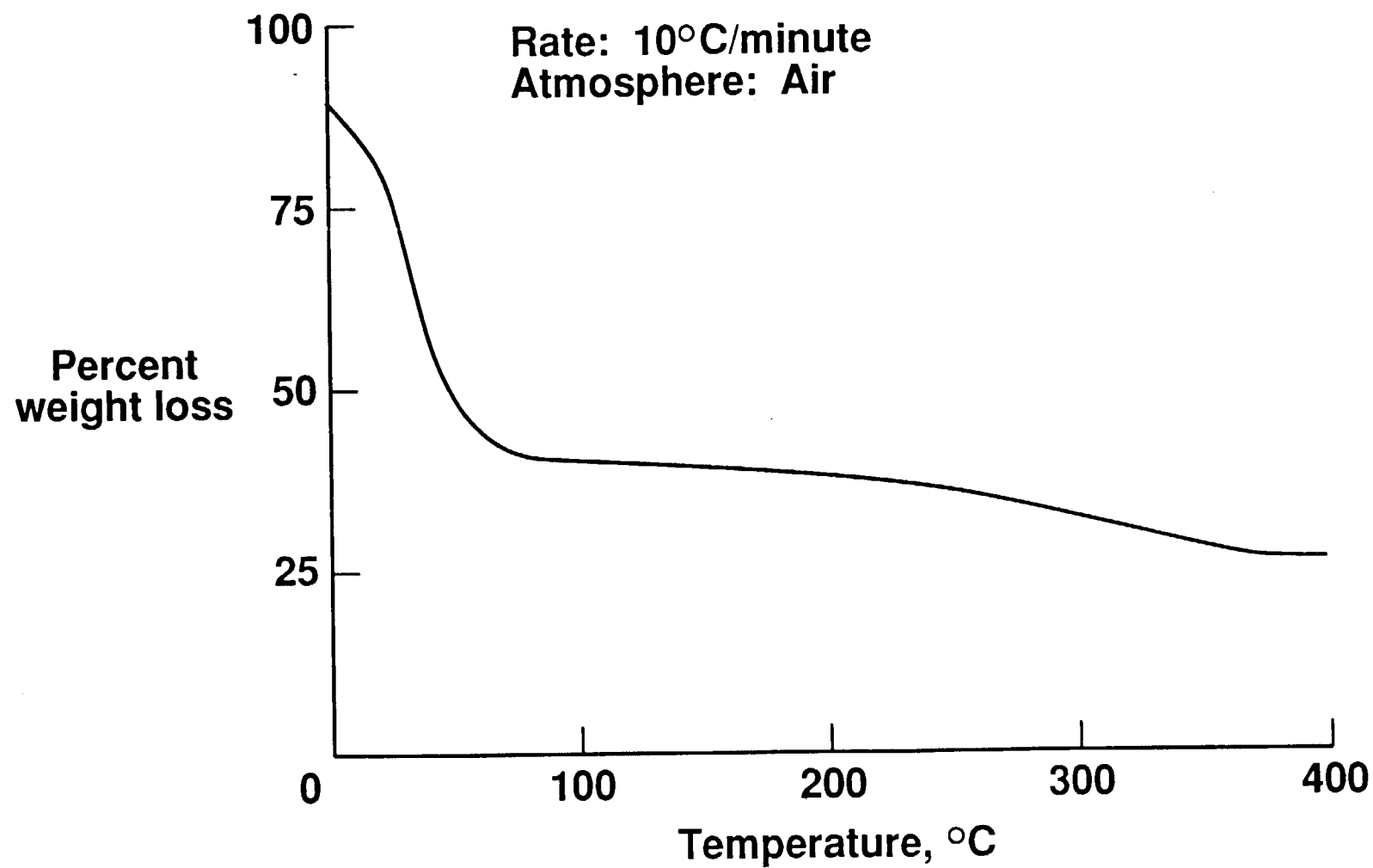


Figure 3. PMHS solution: Preliminary TGA results

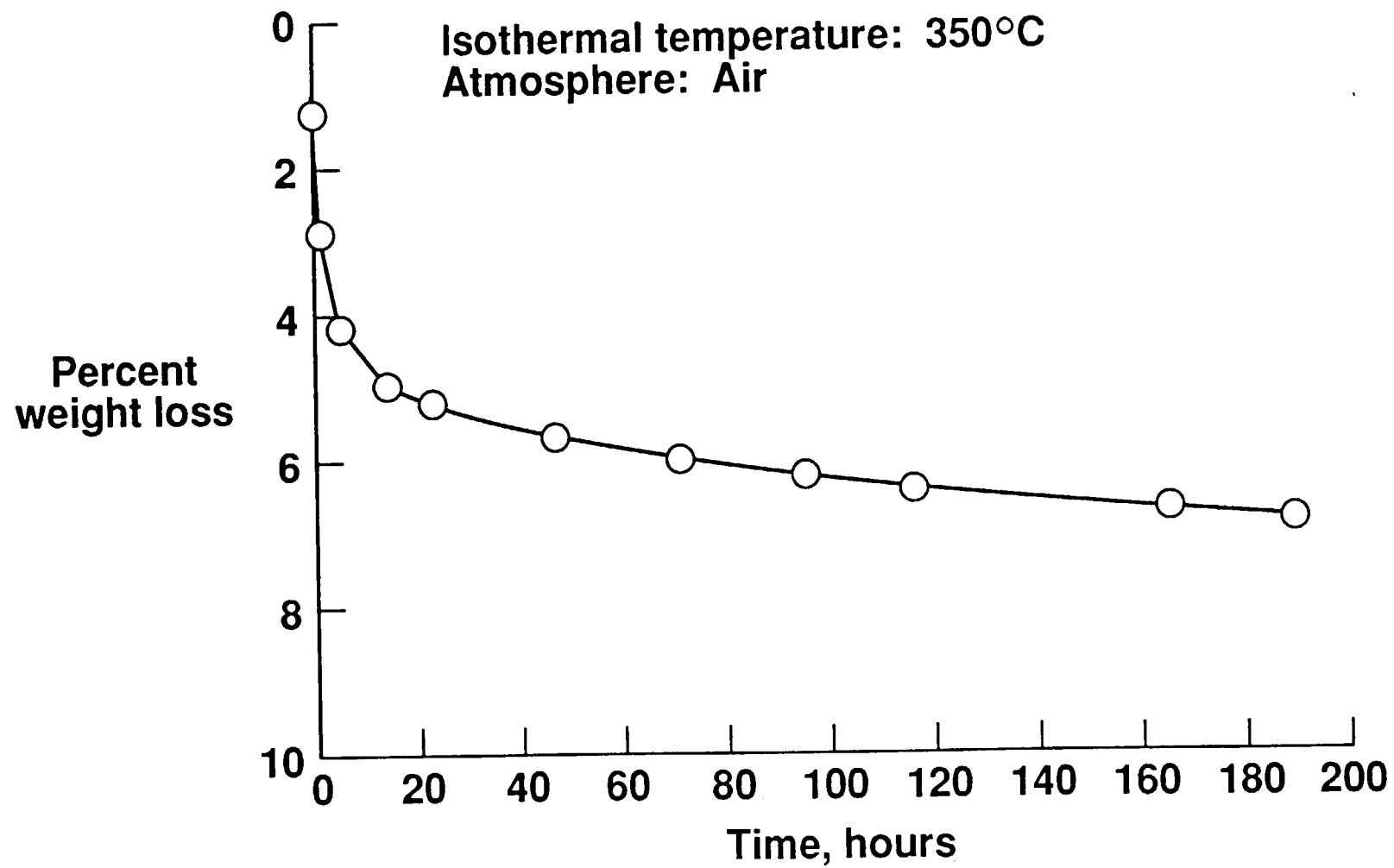


Figure 4. Isothermal TGA results of dry sample

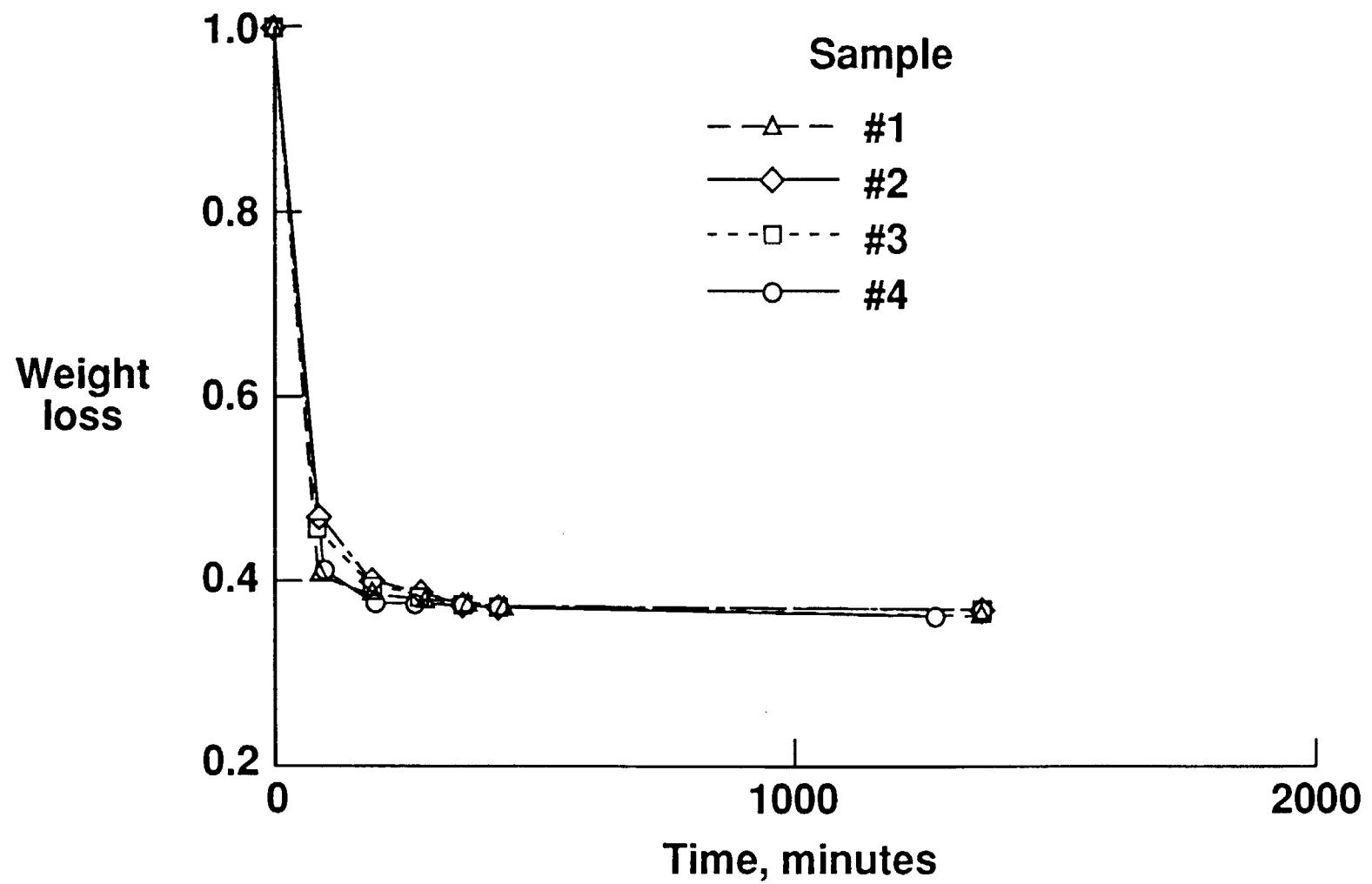


Figure 5. Drying curve for PMHS solution

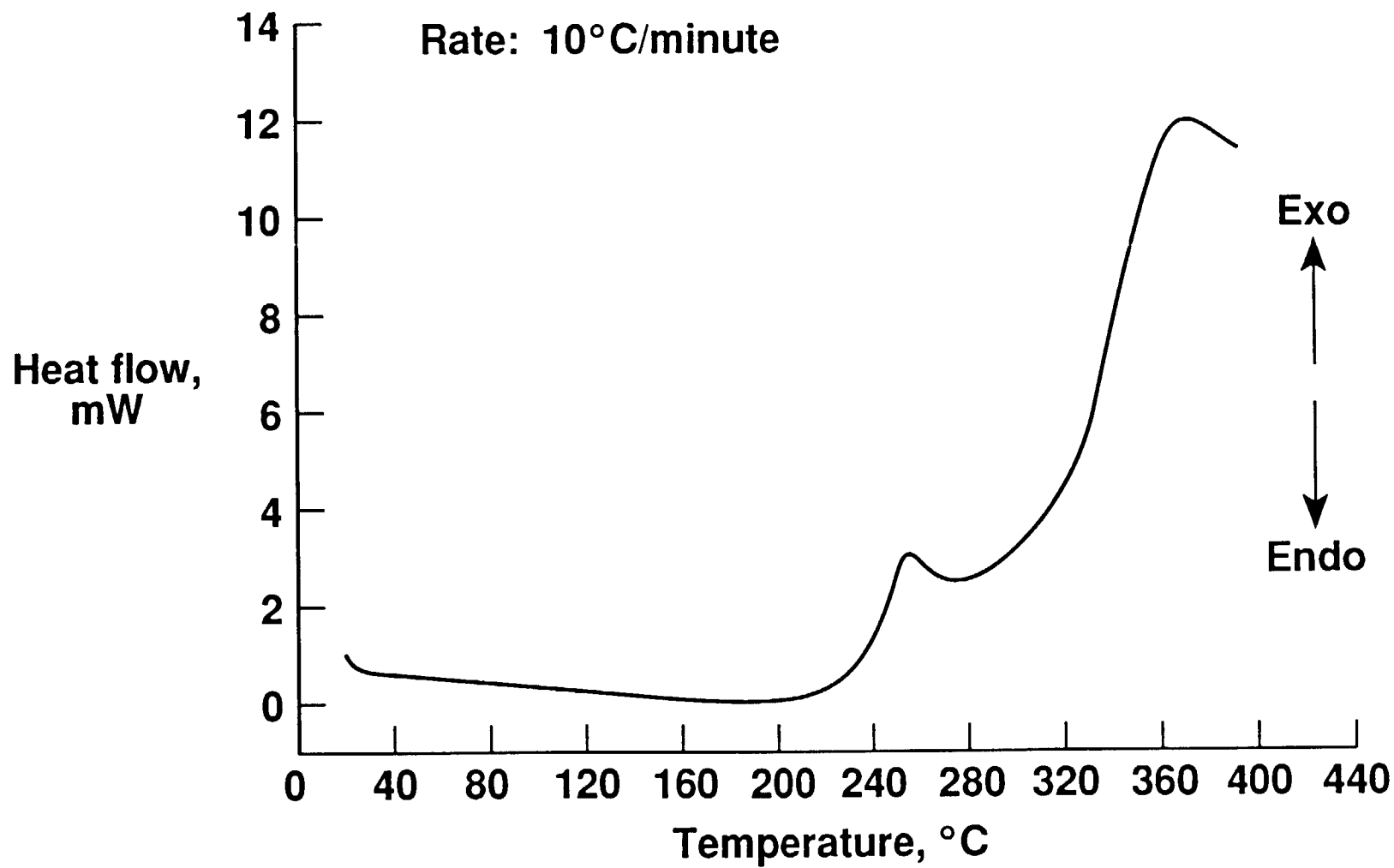


Figure 6. DSC results of air dried sample

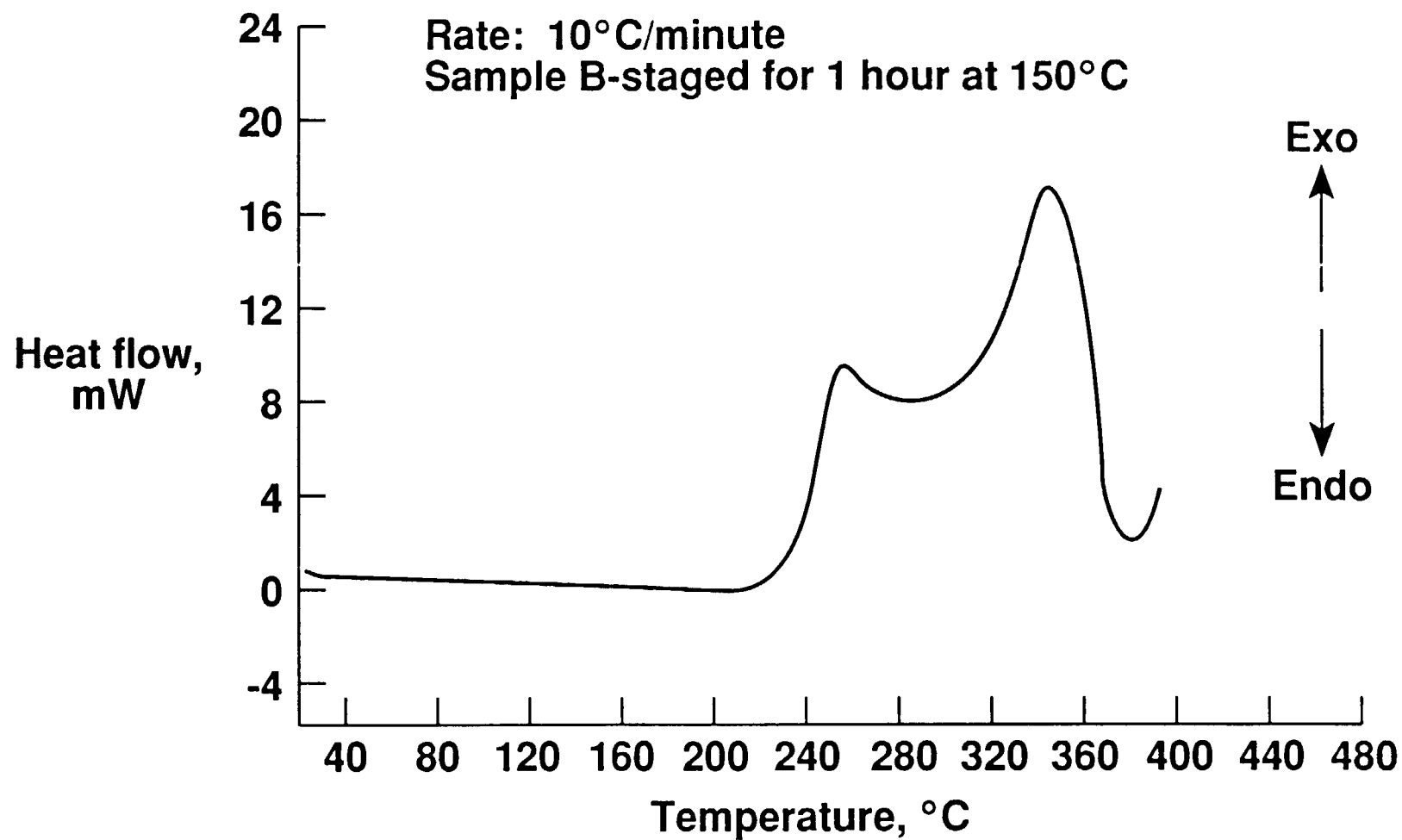


Figure 7. DSC results on B-staged sample

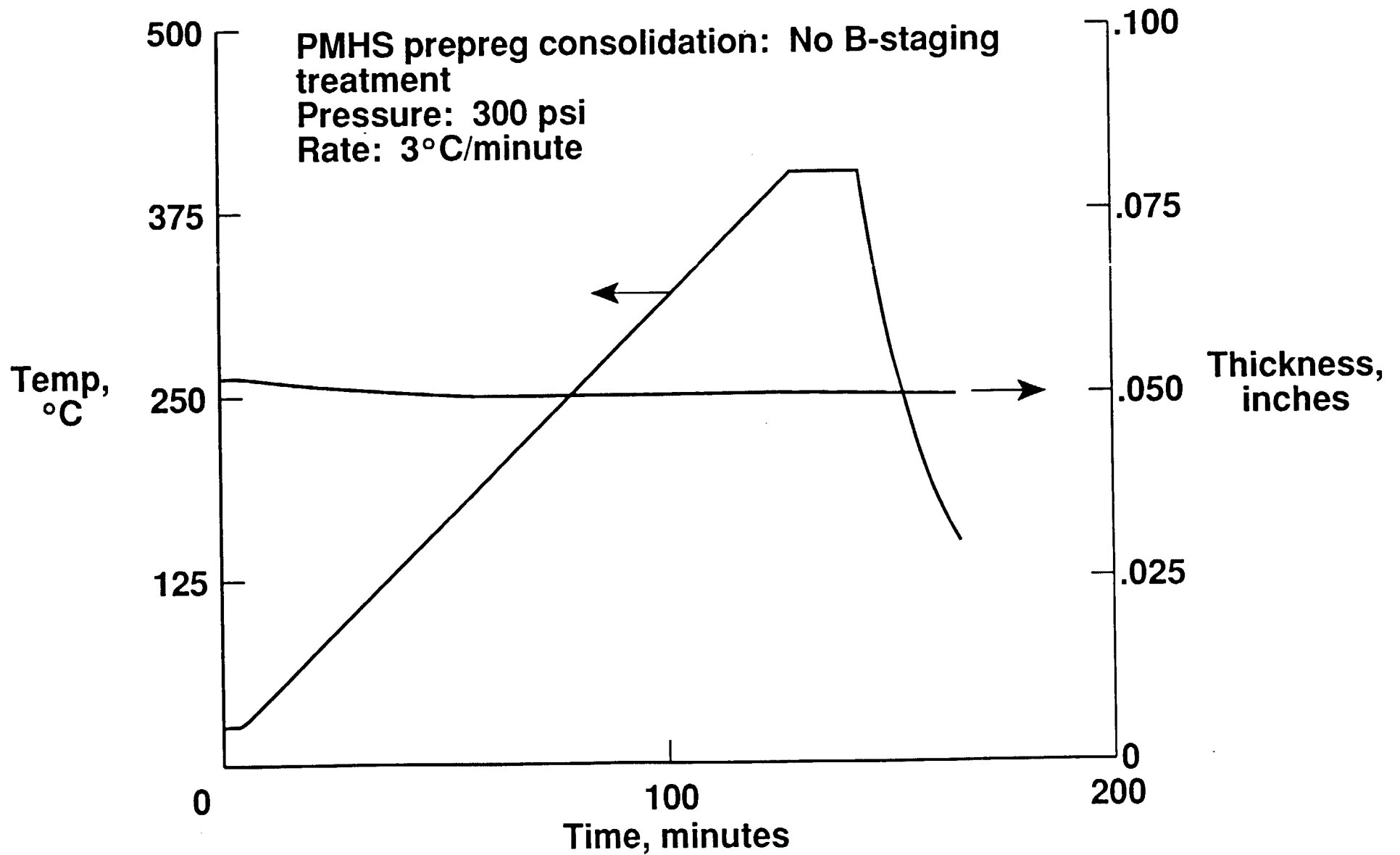


Figure 8. Plastometry of prepreg no subject to heat treatment

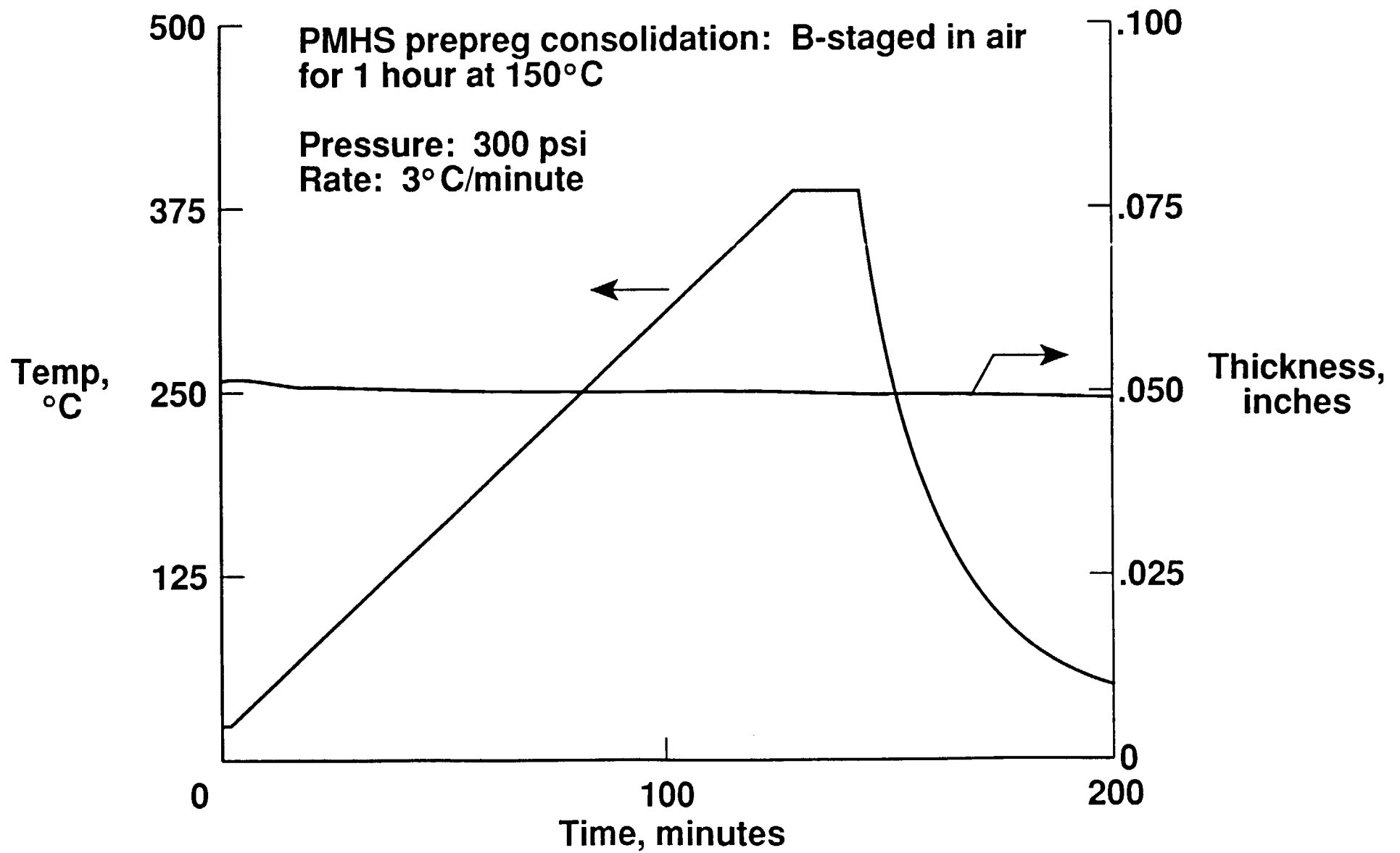
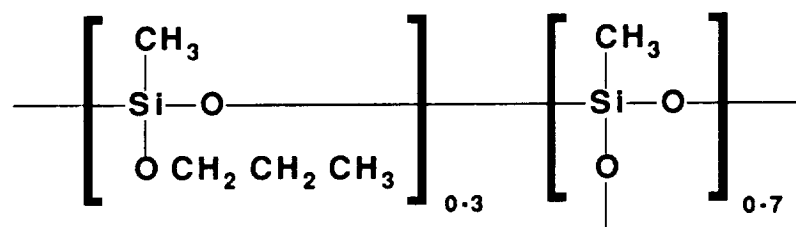
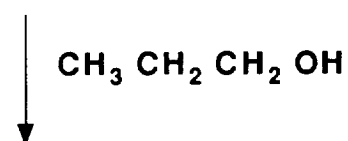
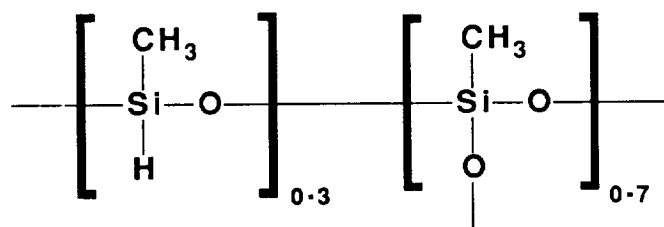
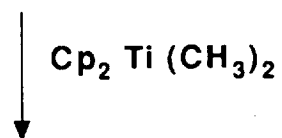
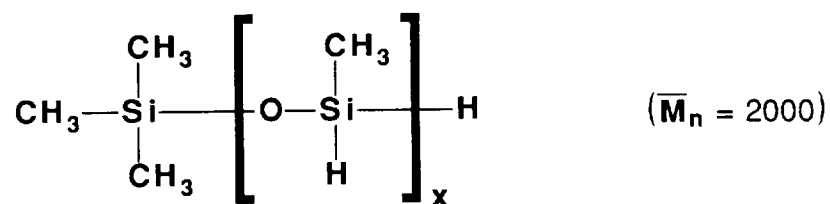


Figure 9. Plastometry of B-staged prepreg

APPENDIX I

PMHS CHEMISTRY SCHEMATIC



APPENDIX II

PMHS PREPREG PROCESS SHEET

Operator CLARENCE STANFIELD Date 7-2-90B

Release Paper HALOGENATED TEFLON SUBSTITUTE (SKINNER) Wt. 45

Resin Solution PMHS (NEW) IN 1 PROH Wt. Before 729 Wt. After 660

Solution Applied 69 Date Resin Made 6-25-90 Die # 5

Graphite HERCULES AB4 12K UNISIZED Wt. Before 551 Wt. After 498

Amt. Graphite Applied 53

Travel Setting Before 0 After 6.625 Travel 6.625

Lead Screw Setting St 12.5 End 12.5 Drum Diameter 23.75

Drum Setting 5.34

Tows Per Inch 5.13

Revolution of Drum 34

Flow Meter Setting

Winding Machine W-25

Prepreg Width 6.625

Solvent Used 1 PROPANOL

Resin Solids Content 41.6 %

Solvent Content 58.4 %

Graphite Fiber Lot # 751-4E

Total Prepreg Wt. 167

Fiber Sizing Data

Run #

Fiber

Sizing Resin

Solvent

% of Sizing in Solution

Sizing % on Fiber

Date Solution MFG.

Comments:

Dry for 45 minutes from Room Temperature to with DRIQUIK UNIT set at 60%Start Stop

Fiber Wt. %	<u>43.44</u>	Applied Wt.	<u>122.00</u>
Resin Solids Wt. %	<u>23.53</u>	Prepreg Wt.	<u>122.00</u>
Prepreg Areal Wt.	<u>35.54</u>	Wt. Loss	<u>0.00</u>
Fiber Areal Wt.	<u>15.44</u>	Prepreg Volatile Wt.	<u>40.30</u>
True Fiber Wt. %	<u>64.87</u>	Prepreg Volatile Wt. %	<u>33.03</u>
True Resin Solids Wt. %	<u>35.13</u>		

Other Comments:

PRECERAMIC POLYMER COMPOSITES

K. Srinivasan* and S. N. Tiwari#

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1. Motivation

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2. Experimental

As mentioned previously, the starting material was an oligomeric copolymer supplied in a solution of 1-Propanol. The material was received in several batches, with varying concentrations of polymer. As prepregging conditions required a 35 % solution of polymer by weight (approximately), a common first step was to concentrate the polymer solution by distilling off calculated amounts of solvent. Brookfield viscosities and densities were routinely measured as a function of solution concentration (Figures 1 and 2).

A preliminary thermogravimetric analysis of the PMHS copolymer was undertaken, using a Perkin Elmer TGS-2, to establish the thermal stability limit of the material. The test was conducted in air at a heating rate of 10 °C/minute, and the result appears in Fig. 3. The solvent is seen to be extremely volatile, as evidenced by the weight loss that occurs in the time interval between the weighing of the specimen and the commencement of the test (approximately five minutes). Upto 100 °C, a weight loss of 59 % is seen, mostly due to solvent loss. Between 100 °C and 375 °C, the rate of weight loss shows a two stage drop, with an inflection at 275 °C. This is presumed to be due to both continued solvent loss and evolution of reaction products. Beyond 375 °C, and at a weight loss of 74 %, the curve is seen to level off. An isothermal TGA run on a dried polymer sample in air at 350 °C also showed a very stable profile upto 200 hours (Fig. 4). This was further confirmed by mass spectrometer results.

Since it is desirable to achieve prepregging at ambient conditions, the next step undertaken was to study the drying characteristics of the PMHS solution in air at room temperature. Several samples of the solution were weighed out and air dried for periods greater than 24 hours. The samples were periodically weighed till a constant weight was observed (Fig. 5). In each case a transparent film was obtained, however these films had a tendency to crack and crumble with passage of time.

These samples were then heated in air ovens at different temperatures (250 °, 285 °, 325 °, 375 ° and 400 °C) for one hour to observe film forming capabilities. However, none of the heat treated samples was

seen to maintain film forming ability, in each case a white powder was obtained.

DSC runs were carried out on each of these samples at the rate of 10 °C/minute in a DuPont 910 DSC. An air dried film, as well as samples heated upto 150 ° and 200 °C were examined. In each case barring for a high temperature exotherm, no transitions characteristic of polymers (such as T_g) were observed. Representative results are shown in Figures 6 and 7. This implied that though some reaction and crosslinking was probably occurring (also confirmed by FTIR results), the material did not soften (or flow) in the temperature regime studied. This has unfortunate consequences regarding processing and consolidation operations.

These results notwithstanding, the PMHS copolymer was solution prepregged via the drum winding technique. Though this apparatus has been described previously [4], a brief description of the process is outlined. An AS-4 (12K, unsized) fiber tow from a free spinning unwinding creel, passes between two tension bars and onto guide spools (that align the fiber) before it enters a sealed resin reservoir. Within the reservoir, the fiber tow passes through the impregnating PMHS/1-Propanol solution over an assembly of rollers. These serve to spread the fibers as it is being impregnated and ensure complete wetout. The tow exits the reservoir through a stainless steel die that squeezes the resin solution through the fiber tow, meters the amount of resin on the fiber and shapes the thickness and width of the impregnated tow. This tow is wound on a 2.5 feet diameter drum wound with a trifluoroethylene polymer release film. The entire creel - guide roll - reservoir assembly is maintained on a moving track whose translational speed is adjusted such that the impregnated tow winds on the drum to provide a continuous gap-free prepreg. The process conditions are given in Appendix 2. II

In order to determine proper B-staging conditions, several pieces of the prepreg were B-staged in air ovens for one hour at the following temperatures: 150 °, 200 °, 250 °, 300 °, 350 ° and 400 °C. These samples were subject to parallel plate plastometer experiments as well as consolidation cycles of temperature and pressure in closed

molds.

In a parallel plate plastometer [5], several unidirectional pieces of prepreg are tacked together and heated between the platens of a press under pressure to determine regimes of flow in the material and hence suitable consolidation conditions. Consolidation was monitored as the thickness change during the heat - pressure cycle. Seven unidirectional pieces sized 5/8 in. by 5/8 in. were used, and the pressure employed was 300 psi. In addition to the B-staged prepreg samples mentioned above, a prepreg sample subject to no heat treatment was also examined in the plastometer. As seen in figures 8 and 9, virtually no flow is seen between room temperature and 400 °C.

The B-staged samples and samples subject to no heat treatment were next subject to lamination in a Pasadena hydraulic compression press. Four 3 in. X 3 in. unidirectional prepreps were tacked together and heated upto various temperatures between 250 °C and 400 °C. A pressure of 300 psi was used during the lamination cycle. Typical hold times ranged from 15 to 30 minutes. None of the samples were seen to be effectively consolidated in the different time - temperature - pressure cycles employed.

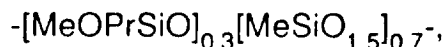
To simultaneously ameliorate the twin problems of the lack of film forming ability and potential brittleness, attempts were made to blend the PMHS copolymer with a thermoplastic polyimide. The resin selected was 5218 from Ciba - Geigy. Prominent among its properties are good toughness and high temperature resistance. Solubility tests of the PMHS copolymer were undertaken in the following solvents (to find a suitable co-solvent) : N, N-dimethyl acetamide (DMAC), N, N-dimethyl formamide (DMF), Methylene chloride, Chloroform, 1, 4-dioxane (Dioxane) and Bis (2-methoxy-ethyl) ether (Diglyme). However, the PMHS copolymer was seen to be insoluble in all these solvents. Attempts were also made to find miscibility of 1-Propanol with these solvents. Solutions of PMHS in 1-Propanol were mixed with those of 5218 in DMAC, DMF, Diglyme etc. In order to preserve the dominant properties of the polysisquioxane polymer in the mixture, the maximum blend ratios attempted were 80% polysisquioxane - 20% 5218. 90 - 10 blends were also attempted. However, in each of the above cases, the two components did not form a homogeneous mixed solution.

3. Conclusions and Recommendations

Despite the attractive high temperature property profile of the Polysilsesquioxane polymer noted in this study, in its present form, several key barriers are seen as preventing its use in composite matrix applications. While the base material (70/30 masked copolymer soluble in propanol) appears to have been rendered suitable for prepregging, the conversion to the insoluble polysilsesquioxane polymer proceeds with no appreciable flow or tack. This fact is perhaps the single greatest detriment, for a failure to soften and / or flow in a low temperature regime (in this case room temperature to 400 °C) provides no avenues for effective consolidation into quality, void free laminates. Further, the tendency of the film to fall apart into a powder must also be viewed with alarm, for to fulfill its role in the composite, the resin must maintain structural and mechanical integrity, throughout the useful temperature range.

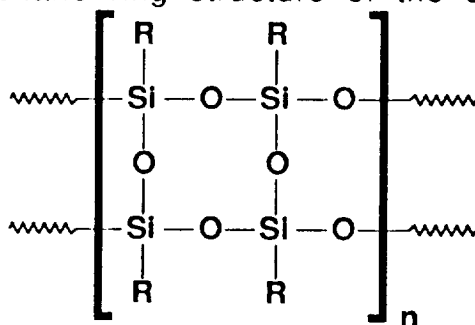
These factors notwithstanding, cost and thermal stability considerations still warrant a continued interest in this system. Several points requiring clarification, modifications and recommendations are now discussed:

1. When the general structure of the PMHS copolymer (starting material) is written as:



it is impossible to determine what a single molecule looks like. By observing a single molecule, one can readily identify potential sites for crosslinking, potential for flow *etc.* Hence it is necessary to determine the hypothesized structure of the starting copolymer, ie. \bar{M}_n or \bar{M}_w of the starting copolymer.

2. The fused tetrasiloxane ring structure of the silsesquioxane:



produces a highly crosslinked structure that may be responsible for the intractable nature of the polymer generated in this study. Several modifications can be suggested to alleviate the problem. Since the above structure is generated from the unit $[\text{MeSiO}_{1.5}]$, and since that unit accounts for 70 % of the starting oligomer, a possible first step may be the reduction of the $[\text{MeSiO}_{1.5}]$ unit, *ie.* effectively increase the extent of $-\text{[MeOPrSiO]}-$ unit in the starting oligomer. Alternatively, a fraction of the $[\text{MeSiO}_{1.5}]$ unit could be chemically modified to reduce its functionality, *ie.* effectively reducing the cross link density in the final polymer. In both cases, not only must the chemistry be altered, but the penalty (in terms of mechanical / thermal properties of the final polymer) must also be assessed.

3. Another potential approach can be to blend / graft small quantities of film formers that can induce the polysilsesquioxane to maintain a continuous resinous network. Depending on the chemistry, these can be in resin or oligomeric / monomeric form. These can be of two basic types:

A. Silicone - Organic Polymers: Silicone - organic copolymers have been made with a variety of organic constituents [6]. Both copolymerization, as well as grafts of prepolymerized segments have been employed. Several such compositions have been used as processing aids and retain many of the excellent properties of silicone polymers. While the list of formulations is extensive and includes polyester, epoxy, phenol-formaldehyde, acrylic and ether based compositions, of importance to us, (in view of thermal and strength / stiffness properties desired), are silicone - polyimide and silicone - polycarbonate formulations. Attempts at copolymerizing or blending small quantities of these may also be attempted.

B. Silsesquioxane - Silicone Polymers: More appealing than silicone - organic copolymeric compositions, are silicone polymer modifications of the PMHS copolymer. Dimethyl, Diphenyl and Phenyl-Methyl siloxane polymers are known to possess outstanding thermal stability and good film forming properties. These resins can also be tailored to a desired property profile through control of cure catalysts and chemistry. These can not only behave as processing aids, but also provide toughness to the brittle polysilsesquioxane systems. Further, blending of the silsesquioxane polymer with silicone systems is likely to prove easier. Consideration of several factors favours the biphenyl polymer for the blending experiments. These resins possess the most

miscibility, are least brittle, have the best tack and are most thermally resistant. Further, cure chemistry can also be better controlled.

4. Finally, no discussion will be complete without a consideration of other preceramic systems. These can be broadly classified as [7]: Silicon - Carbon systems, Silicon - Nitrogen systems, Silicon - Carbon - Nitrogen systems, Silicon - Carbon - Oxygen systems and other precursor systems. Most promising among the Silicon based systems are the Polycarbosilanes. These include polymers containing both the Si - C- Si and Si - (C)_x - Si backbone. PCS-I and PCS-II are commercially available materials with an average \overline{M}_n of 1000 - 2000 and are soluble in several common organic solvents. They possess attractive thermal and mechanical properties. In the US these are available from Dow Corning, (for development purposes only), at \$ 400/kg. The search for suitable low temperature polymer fabrication routes to the ceramics of boron, aluminum and some transition metals also reveals some promising preceramic polymers such as borosiloxane polymers, carborane - siloxane polymers, boron -nitrogen polymers and organometallic aluminum and transition metal systems. Recently [8], semi-amorphous networks of sodium, potassium, lithium and magnesium silico-aluminates, (termed geopolymers), have been suggested as low temperature processible matrices for composite materials.

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1. The first step is to identify the problem or question that needs to be answered. This involves understanding the context and the specific requirements of the task.